Preparation and Solid-State Isomerization of *Se,Se'*-Dialkyltetraphenyldiphosphadiselenatetrazocines: X-ray Structures of 1,5-$Ph_4P_2N_4Se_2Me_2$ and $[Ph_2P(NH_2)_2]_2Se$

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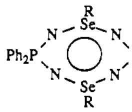
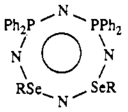
The reaction of the $Ph_2PN_2(SiMe_3)_3$ with organoselenium trichlorides $RSeCl_3$ in acetonitrile at 23 °C produces high yields of 1,5-$Ph_4P_2N_4Se_2R_2$ (**1a**, R = Me; **1b**, R = Et; **1c**, R = Ph) and, for **1a,b**, small amounts of 1,5-$Ph_4P_2N_4Se_2$. These heterocycles were characterized by ^1H, ^{31}P, and ^{77}Se NMR, IR, and mass spectroscopies and, in the case of **1a**, by X-ray crystallography, which showed that the eight-membered $P_2N_4Se_2$ ring adopts a chair conformation. Crystals of **1a** are triclinic, space group $P\bar{1}$, with $a = 8.697(2)$ Å, $b = 8.934(2)$ Å, $c = 10.163(2)$ Å, $\alpha = 81.36(2)°$, $\beta = 68.46(1)°$, $\gamma = 65.69(2)°$, $V = 669.3$ Å^3, and $Z = 1$. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.073$ and $R_w = 0.044$ for 3513 observed reflections. The derivatives **1a,b** (but not **1c**) undergo a remarkable solid-state transformation at room temperature under a nitrogen atmosphere to give 1,3-$Ph_4P_2N_4Se_2Me_2$, **2a**, and 1,3-$Ph_4P_2N_4Se_2Et_2$, **2b**, respectively, and, subsequently, small amounts of the Se-dealkylated product 1,3-$Ph_4P_2N_4Se_2$. The compounds **2a,b** were characterized by ^1H, ^{31}P, and ^{77}Se NMR, IR, and mass spectroscopies. A possible mechanism for the isomerization process (**1a**/**1b** → **2a**/**2b**) is discussed. The thermolysis of **1c** in the solid state produces Ph_2Se_2 and cyclophosphazenes, while decomposition of **1a–c** in boiling toluene gives rise to R_2Se_2 (R = Me, Et, Ph) and $Ph_2P(NH)(NH_2)$. After several weeks these toluene solutions produce $[Ph_2P(NH_2)_2]_2Se$, **5**, in which the selenide ion is shown by X-ray crystallography to participate in strong Se–HN hydrogen bonding to four different cations. The crystals of **5** are monoclinic, space group $P2_1/a$ with $a = 9.554(2)$ Å, $b = 21.382(8)$ Å, $c = 12.392(6)$ Å, $\beta = 101.91(3)°$, $V = 2477(1)$ Å^3, and $Z = 4$. The final R and R_w values were 0.087 and 0.093, respectively, for 3299 observed data.

Introduction

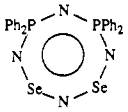
Recent studies have revealed subtle, but significant, differences between the structures,[1a,b] properties,[1c] stabilities,[2] and reactivities[3] of cyclic selenium–nitrogen (Se–N) compounds compared to those of their sulfur analogues. A few years ago we described, in a preliminary communication,[4] the synthesis of *Se,Se'*-diorganotetraphenyldiphosphadiselenatetrazocines, 1,5-$Ph_4P_2N_4Se_2R_2$ (**1a**, R = Me; **1b**, R = Et; **1c**, R = Ph). We now report that **1a,b** undergo a remarkable transformation *in the solid state* at 23 °C to produce the 1,3-isomers **2a,b** together with a small amount of the Se-dealkylated product 1,3-$Ph_4P_2N_4Se_2$, **3**. Full details of the synthesis of **1a–c**, the X-ray structure of **1a**, the solid state isomerization of **1a** and **1b**, the spectroscopic characterization of **2a** and **2b**, and the thermal decomposition of **1a** in the solid state and **1a-c** in solution are presented. The X-ray structure of $[Ph_2P(NH_2)_2]_2Se$, which is formed when **1a** decomposes in boiling toluene, is also described.



1a (R = Me)
1b (R = Et)
1c (R = Ph)



2a (R = Me)
2b (R = Et)



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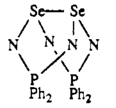

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Experimental Section

The reagents $Ph_2PN_2(SiMe_3)_3$, $Me_2PN_2(SiMe_3)_3$, and Me(Ph)-$PN_2(SiMe_3)_3$ were prepared from the appropriate $R_2PN(SiMe_3)_2$ derivative and Me_3SiN_3 by using the procedure described for Me(Ph)-$PN_2(SiMe_3)_2$.[5] The organoselenium trichlorides were prepared from the corresponding diselenides RSeSeR by the literature method.[6] Dimethyl diselenide, diethyl diselenide, diphenyl diselenide, and trimethylsilyl azide were all commercial products, which were used as received.

All manipulations were carried out under a dry atmosphere of purified nitrogen (Ridox, P_2O_5, silica). Acetonitrile was freshly distilled over first CaH_2, then P_2O_5, and finally CaH_2 again. Diethyl ether was distilled from Na/benzophenone. Dichloromethane was distilled from P_2O_5. Toluene was distilled from Na/benzophenone. Distillations were performed under nitrogen. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by the Canadian Microanalytical Service, Vancouver, BC, Canada.

Instrumentation. Infrared spectra were recorded as Nujol mulls with KBr windows on a Nicolet 5DX FT-IR spectrometer. ^{31}P NMR spectra were obtained either on a Varian XL200 spectrometer, or on a Bruker AM400 spectrometer, using external 85% H_3PO_4 as reference. ^1H NMR spectra were determined on a Bruker ACE200 spectrometer using various deuterated solvents as internal reference. ^{77}Se NMR spectra were recorded on a Bruker AM400 spectrometer using PhSeSePh in $CDCl_3$ as external reference assigned at +461 ppm relative to Me_2Se (0 ppm). Electron impact mass spectra were recorded by using a Kratos MS80RFA instrument set at 70 eV. Fast atom bombardment mass spectra were provided by the Institute of Sedimentary and Petroleum Geology, Calgary, Canada.

Preparation of 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Ph, Me, Et). The procedure and observations for the preparation of these derivatives were similar and

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Table I. ^{1}H, ^{31}P, and ^{77}Se NMR Data (δ) for 1,3-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et) and 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et, Ph)

	^{1}H^a	^{31}P^b	^{77}Se^c
1,5-$Ph_4P_2N_4Se_2Me_2$ (**1a**)	2.82 (s, 6H), 7.3–8.0 (m, 20H)	31.7	888 [t, $^2J(^{31}P\text{-}^{77}Se)$ = 86.5 Hz]^d
1,5-$Ph_4P_2N_4Se_2Et_2$ (**1b**)	1.40 (t, 6H), 3.15 (q, 4H), 7.3–8.0 (m, 20H)	32.5^d	896 [t, $^2J(^{31}P\text{–}^{77}Se)$ = 61.0 Hz]
1,5-$Ph_4P_2N_4Se_2Ph_2$ (**1c**)	7.3–8.0 (m)	33.6	*e*
1,3-$Ph_4P_2N_4Se_2Me_2$ (**2a**)	2.83 (s, 6H), 7.3–8.0 (m, 20H)	20.4	844^f
1,3-$Ph_4P_2N_4Se_2Et_2$ (**2b**)	1.41 (t, 6H), 3.14 (q, 4H), 7.2–8.0 (m, 20H)	21.3	869^f

^{a} s, singlet; t, triplet; q, quartet; m, multiplet. ^{b} Relative to external 85% H_3PO_4. ^{c} Relative to Me_2Se (0 ppm). ^{d} Corrected value (cf. ref 4). ^{e} Not determined due to low solubility. ^{f} Poorly resolved virtual triplet.

are only described in detail for **1c**. The ^{1}H, ^{31}P, and ^{77}Se NMR data for **1a–c** and **2a,b** are summarized in Table I.

1,5-$Ph_4P_2N_4Se_2Ph_2$, 1c. A solution of $Ph_2PN_2(SiMe_3)_3$ (2.94 g, 6.80 mmol) in acetonitrile (125 mL) was added dropwise (90 min), with stirring, to a yellow solution of phenylselenium trichloride (1.78 g, 6.80 mmol) in acetonitrile (150 mL) at 23 °C by cannula. After ca. one-third of the addition the color of the solution had intensified to golden yellow and, upon further addition of the phosphorus(V) reagent, it became paler yellow and a white precipitate was deposited. After 16 h this precipitate was separated by filtration (filter cannula), washed with acetonitrile (2 × 30 mL), dried under vacuum, and identified as 1,5-$Ph_4P_2N_4Se_2Ph_2$ (2.30 g, 3.10 mmol, 91%), mp 225–230 °C (decomposition to a red melt). Anal. Calcd for $C_{36}H_{30}N_4P_2Se_2$: C, 58.54; H, 4.10; N, 7.59. Found: C, 58.85; H, 4.27; N, 7.44. IR (cm^{-1}): 1445 (w), 1109 (m), 1081 (s), 1060 (s), 1025 (w), 1001 (w), 968 (s), 955 (m), 782 (vw), 748 (w), 743 (w), 698 (m), 691 (m), 684 (m), 669 (m), 536 (s), 527 (s).

1,5-$Ph_4P_2N_4Se_2Me_2$, 1a. The reaction of $Ph_2PN_2(SiMe_3)_3$ (7.10 g, 16.4 mmol) with $MeSeCl_3$ (3.30 g, 16.5 mmol) in acetonitrile (325 mL) at 23 °C produced 1,5-$Ph_4P_2N_4Se_2Me_2$ (2.80 g, 4.55 mmol, 56%) as a white solid, mp 164–168 °C (decomposition to a red melt). Anal. Calcd for $C_{26}H_{26}N_4P_2Se_2$: C, 50.82; H, 4.27; N, 9.12. Found: C, 49.17; H, 4.38; N, 8.66. IR (cm^{-1}): 1401 (w), 1110 (s), 1088 (m), 1061 (m), 970 (vs), 898 (s), 753 (w), 697 (m), 667 (w), 597 (w), 538 (m), 526 (m). FAB–MS: M^+ at *m/e* 616 (with the appropriate isotopic distribution for two Se atoms). EI-MS (70 eV) [*m/e* (%)]: 188 (75, $MeSeSeMe^+$), 108 (33, $MeSeMe^+$), 94 (90, $MeSe^+$), 77 (100, Ph^+).

The yellow acetonitrile filtrate was reduced in volume to ca. 50 mL and was left to stand at room temperature for 36 h. The resultant yellow needles were separated by using a filter cannula, washed once with acetonitrile (ca. 20 mL), dried in vacuo, and identified as 1,5-$Ph_4P_2N_4Se_2$, (0.52 g, 0.89 mmol, 11%). Anal. Calcd for $C_{24}H_{20}N_4P_2Se_2$: C, 49.33; H, 3.46; N, 9.59. Found: C, 48.82; H, 3.50; N, 9.30. IR (cm^{-1}): 1435 (s), 1120 (s), 1112 (s), 1032 (m), 1016 (m), 999 (w), 987 (m), 957 (vs), 858 (w), 850 (w), 751 (m), 693 (s), 672 (s), 628 (m), 620 (m), 536 (s), 513 (s), 508 (s). ^{1}H NMR (in $CDCl_3$): δ 7.3–8.0 (m). ^{31}P NMR (in CH_2Cl_2): δ 113.4 ppm [^2J(P–Se) = 80.6 Hz]. ^{77}Se NMR (in CH_2Cl_2): δ 1066 ppm [t, ^2J(P–Se) = 81.6 Hz]. FAB–MS: M^+ at *m/e* 586 (with the appropriate isotopic distribution for two Se atoms).

1,5-$Ph_4P_2N_4Se_2Et_2$, 1b. The reaction of $Ph_2PN_2(SiMe_3)_3$ (7.36 g, 17.0 mmol) with $EtSeCl_3$ (3.66 g, 17.1 mmol) in acetonitrile (325 mL) at 23 °C produced 1,5-$Ph_4P_2N_4Se_2Et_2$ (4.70 g, 7.30 mmol, 86%) as a white solid, mp 148–155 °C (decomposition to a red melt). Anal. Calcd for $C_{28}H_{30}N_4P_2Se_2$: C, 52.34; H, 4.72; N, 8.72. Found: C, 51.70; H, 4.53; N, 8.58. IR (cm^{-1}); 1478 (w), 1436 (w), 1409 (m), 1310 (w), 1215 (m), 1108 (vs), 1094 (vs), 1062 (m), 1046 (m), 1027 (w), 999 (w), 990 (vw), 996 (s), 949 (vs), 753 (s), 699 (s), 669 (m), 603 (m), 533 (vs). EI-MS (70 eV) [*m/e* (%)]: 216 (100, $EtSeSeEt^+$), 137 (44, $EtSeEt^+$), 108 (35, $EtSe^+$), 77 (48, Ph^+).

The yellow acetonitrile filtrate was reduced in volume to ca. 50 mL and was left to stand at room temperature for 36 h. The resultant yellow needles were isolated, washed once with acetonitrile (ca. 20 mL), dried in vacuo, and identified as 1,5-$Ph_4P_2N_4Se_2$ (0.35 g, 0.60 mmol, 7%) by comparison of ^{31}P NMR and IR spectra with those of an authentic sample.

Reaction of $RR'PN_2(SiMe_3)_3$ with $PhSeCl_3$ (R = R' = Me; R = Me, R' = Ph). A solution of $Me_2PN_2(SiMe_3)_3$ (1.55 g, 5.0 mmol) in acetonitrile (50 mL) was added dropwise (75 min), with stirring, to a solution of $PhSeCl_3$ (1.32 g, 5.0 mmol) in acetonitrile (150 mL). After 16 h the bright yellow solution was reduced in volume to 50 mL and stored at –20 °C for 2 days to give bright yellow crystals of diphenyl diselenide (1.52 g, 4.9 mmol, 98%) identified by comparison of the IR spectrum with that of an authentic sample. The ^{31}P NMR spectrum of the reaction mixture revealed a large number of resonances in the 0–40 ppm range.

In a similar manner the reaction of $Me(Ph)PN_2(SiMe_3)_3$ (7.24 g, 19.4 mmol) with $PhSeCl_3$ (5.09 g, 19.4 mmol) in acetonitrile (360 mL) produced diphenyl diselenide (6.04 g, 19.4 mmol, 100%).

Solid-State Isomerization and Dealkylation of 1,5-$Ph_4P_2N_4Se_2Me_2$, 1a. Solid 1,5-$Ph_4P_2N_4Se_2Me_2$ (1.47 g, 2.40 mmol) was stored in the dry nitrogen atmosphere of a glovebox for 6 weeks. During this time the color of the solid changed from white to peach. The solid was then extracted with acetonitrile (3 × 30 mL). Solvent was removed from the combined yellow-green acetonitrile extracts under vacuum, and the resultant yellow solid was identified as 1,3-$Ph_4P_2N_4Se_2$ (0.17 g, 0.29 mmol, 12%). Anal. Calcd for $C_{24}H_{20}N_4P_2Se_2$: C, 49.33; H, 3.46; N, 9.59. Found: C, 49.21; H, 3.41; N, 9.46. IR (cm^{-1}): 1483 (s), 1458 (vs), 1437 (vs), 1310 (m), 1185 (vs), 1170 (s), 1125 (s), 1108 (s), 1070 (m), 1027 (m), 996 (s), 915 (s), 754 (vs), 695 (vs), 536 (vs), 519 (s), 515 (s), 496 (s), 490 (s). ^{1}H NMR (in $CDCl_3$): δ 7.3–8.0 (m). ^{31}P NMR (in CH_3CN): δ 18.5 ppm (s). ^{77}Se NMR (in CH_3CN): δ 1356 ppm (m).

The peach-colored acetonitrile insoluble material was dried in vacuo and identified as 1,3-$Ph_4P_2N_4Se_2Me_2$ (1.29 g, 2.1 mmol, 88%). Anal. Calcd for $C_{26}H_{26}N_4P_2Se_2$: C, 50.82; H, 4.27; N, 9.12. Found: C, 50.19; H, 4.28; N, 8.83. IR (cm^{-1}): 1481 (m), 1437 (vs), 1404 (w), 1336 (w), 1309 (w), 1166 (vs), 1153 (vs), 1129 (vs), 1110 (m), 1068 (m), 1042 (s), 1036 (m), 998 (m), 915 (s), 755 (s), 721 (s), 696 (s), 563 (s), 540 (m), 520 (s), 425 (w). FAB–MS: M^+ at *m/e* 616 with the appropriate isotopic distribution for two Se atoms. EI-MS (70 eV) [*m/e* (%)]: 188 (100, $MeSeSeMe^+$), 109 (23, $MeSeMe^+$), 94 (87, $MeSe^+$), 77 (25, Ph^+).

Solid-State Isomerization and Dealkylation of 1,5-$Ph_4P_2N_4Se_2Et_2$, 1b. Solid 1,5-$Ph_4P_2N_4Se_2Et_2$ (1.40 g, 2.20 mmol) was stored in the dry nitrogen atmosphere of a glovebox for 12 weeks. During this time the color of the solid changed from white to peach. The solid was then extracted with acetonitrile (3 × 30 mL). Solvent was removed from the combined yellow-green extracts under vacuum, and the resultant yellow solid was identified as 1,3-$Ph_4P_2N_4Se_2$ (0.08 g, 0.14 mmol, 6%) by comparison of IR and ^{31}P NMR spectra with those of an authentic sample.

The peach-colored, acetonitrile-insoluble material was dried in vacuo and identified as 1,3-$Ph_4P_2N_4Se_2Et_2$ (1.32 g, 2.1 mol, 94%). Anal. Calcd for $C_{28}H_{30}N_4P_2Se_2$: C, 52.34; H, 4.72; N, 8.72. Found: C, 51.73; H, 4.58; N, 8.64. IR (cm^{-1}): 1461 (m), 1377 (vs), 1310 (w), 1170 (vs), 1158 (s), 1126 (m), 1108 (w), 1068 (w), 1043 (w), 1023 (w), 996 (m), 974 (s), 933 (w), 913 (m), 890 (s), 755 (s), 697 (s), 534 (m), 519 (s). EI-MS (70 eV) [*m/e* (%)]: 216 (100, $EtSeSeEt^+$), 137 (41, $EtSeEt^+$), 108 (75, $EtSe^+$), 77 (33, Ph^+).

Solid-State Thermal Decomposition of 1,5-$Ph_4P_2N_4Se_2Ph_2$, 1c. A sample of 1,5-$Ph_4P_2N_4Se_2Ph_2$ (0.61 g, 0.83 mmol) in a Schlenk tube was heated (oil bath) at 120 °C for 24 h without significant change (^{31}P NMR spectroscopy). Further heating at 140 °C for 1 week produced a yellow sublimate identified as diphenyl diselenide (0.24 g, 0.77 mmol, 92%) by comparison of the IR spectrum with that of an authentic sample. Extraction of the residue with dichloromethane gave a white solid. EI-MS (70 eV): *m/e* 597 [$(Ph_2PN)_3^+$]. ^{31}P NMR (in CH_2Cl_2): +17.0 and +8.3 ppm.

X-ray Structural Analysis of 1,5-$Ph_4P_2N_4Se_2Me_2$, 1a. Crystals of **1a** were obtained by recrystallization from dichloromethane at 0 °C. A suitable transparent block-shaped crystal of **1a** (0.23 × 0.37 × 0.31 mm) was glued to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $10.48 < \theta < 15.78°$. Reduced cell calculations did not indicate any higher metric symmetry. Crystal and instrumental instability were monitored through the measurement of 3 standard reflections every 1 h of X-ray exposure time; there was no indication of crystal decomposition. The net intensities of the data were corrected for reflection width, scale variation, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics. Crystal data and experimental details of the structure determination are compiled in Table II.

Table II. Crystallographic Data for 1,5-$Ph_4P_2N_4Se_2Me_2$, **1a**

chem formula $C_{26}H_{26}N_4P_2Se_2$
$a = 8.697(2)$ Å
$b = 8.934(2)$ Å
$c = 10.163(2)$ Å
$\alpha = 81.36(2)°$
$\beta = 68.46(1)°$
$\gamma = 65.69(1)°$
$V = 669.31$ Å^3
$Z = 1$
fw 614.4
space group $P\bar{1}$
$T = 23(2)$ °C
$\lambda = 0.710\,69$ Å
$\rho_{calcd} = 1.524$ g cm^{-3}
$\mu = 28.42$ cm^{-1}
$R = 0.073$
$R_w = 0.044$

Table III. Atom Coordinates for 1,5-$Ph_4P_2N_4Se_2Me_2$, **1a**

atom	x	y	z	10^3U_{eq}, Å^2
Se(1)	0.62109(5)	0.44196(4)	0.13020(4)	44.9
P(1)	0.2720(1)	0.6886(1)	0.1476(1)	43.4
N(1)	0.3843(4)	0.5210(3)	0.2144(3)	50.6
N(2)	0.6689(4)	0.2817(3)	0.0187(3)	49.9
C(11)	0.0460(5)	0.6958(4)	0.2216(4)	46.1
C(12)	−0.0019(5)	0.5860(5)	0.3225(4)	66.0
C(13)	−0.1775(6)	0.5971(6)	0.3791(5)	80.0
C(14)	−0.3047(6)	0.7148(6)	0.3351(5)	83.1
C(15)	−0.2635(6)	0.8271(7)	0.2389(6)	93.7
C(16)	−0.0900(6)	0.8177(5)	0.1812(4)	73.6
C(21)	0.2595(4)	0.8707(4)	0.2167(4)	46.3
C(22)	0.2890(5)	0.9984(5)	0.1310(5)	68.0
C(23)	0.2846(6)	1.1332(5)	0.1883(6)	91.6
C(24)	0.2544(6)	1.1372(6)	0.3278(6)	84.3
C(25)	0.2221(6)	1.0154(6)	0.4140(5)	79.7
C(26)	0.2251(5)	0.8809(5)	0.3594(4)	62.3
C(1)	0.6709(6)	0.3024(5)	0.2842(4)	74.1

Table IV. Crystallographic Data for $[Ph_2P(NH)_2]_2Se$ **5**

chem formula $C_{24}H_{28}P_2N_4Se$
$a = 9.554(2)$ Å
$b = 21.382(8)$ Å
$c = 12.392(6)$ Å
$\beta = 101.91(3)°$
$V = 2477(1)$ Å^3
$Z = 4$
$T = 165$ K
fw 513.42
space group $P2_1/a$ (No. 14)
$\lambda = 0.710\,69$ Å
$\rho_{calcd} = 1.377$ g cm^{-3}
$\mu = 16.64$ cm^{-1}
$R = 0.087$
$R_w = 0.093$

Table V. Atom Coordinates (×10^4) for $[Ph_2P(NH_2)_2]_2Se$, **5**

atom	x	y	z	10^3U_{eq},^{a} Å^2
Se(1)^b	97(1)	1973(1)	6000(1)	36(1)
Se(2)^b	8548(1)	2032(1)	685(1)	33(1)
P(1)	4370(1)	1729(1)	8344(1)	15(1)
P(2)	6129(1)	1740(1)	3336(1)	15(1)
N(1)	5408(5)	2214(2)	9152(4)	20(2)
N(2)	3301(5)	2139(2)	7431(4)	22(2)
N(3)	6869(5)	2089(2)	4468(4)	23(2)
N(4)	6012(5)	2058(2)	2139(4)	22(2)
C(11)	3277(3)	1253(2)	9040(3)	19(3)
C(12)	1815(3)	1356(2)	8944(3)	23(3)
C(13)	1048(3)	1007(2)	9576(3)	32(3)
C(14)	1743(3)	553(2)	10303(3)	32(3)
C(15)	3205(3)	450(2)	10399(3)	33(3)
C(16)	3972(3)	800(2)	9767(3)	29(3)
C(21)	5535(3)	1210(2)	7799(3)	16(2)
C(22)	4970(3)	651(2)	7316(3)	23(3)
C(23)	5842(3)	236(2)	6887(3)	32(3)
C(24)	7279(3)	381(2)	6940(3)	30(3)
C(25)	7843(3)	940(2)	7423(3)	35(3)
C(26)	6972(3)	1355(2)	7853(3)	31(3)
C(31)	7172(4)	1046(2)	3299(2)	17(2)
C(32)	7512(4)	824(2)	2325(2)	24(3)
C(33)	8278(4)	268(2)	2331(2)	30(3)
C(34)	8704(4)	−66(2)	3311(2)	29(3)
C(35)	8365(4)	155(2)	4284(2)	27(3)
C(36)	7599(4)	711(2)	4278(2)	23(3)
C(41)	4337(3)	1573(2)	3468(2)	16(2)
C(42)	4080(3)	1453(2)	4517(2)	22(3)
C(43)	2700(3)	1310(2)	4647(2)	26(3)
C(44)	1577(3)	1287(2)	3729(2)	26(3)
C(45)	1833(3)	1406(2)	2680(2)	23(3)
C(46)	3213(3)	1550(2)	2550(2)	21(3)

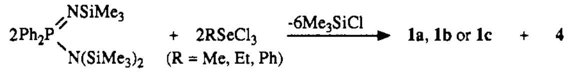
^{a} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. ^{b} Se is disordered over two sites with equal occupancy factors.

The PNSe ring was located in an E map with phases derived from symbolic addition.[7] The remaining non-hydrogen atoms were located in difference maps after refining the scale and thermal parameters. At this stage of the refinement all of the hydrogen atoms were located in difference Fourier maps. All non-hydrogen atoms were refined anisotropically, with the hydrogens calculated with fixed isotropic temperature factors and not refined. The data were corrected for absorption using DIFABS[8] after isotropic refinement. Convergence was reached at $R = 0.073$. The final values of the refined positional parameters are presented in Table III. Tables of hydrogen atom positions and thermal parameters and comprehensive lists of bond distances and angles are available as supplementary material for this paper. Neutral-atom scattering factors for non-hydrogen atoms were used.[9] Scattering factors for H-atoms were taken from ref 10, and anomalous dispersion corrections were applied.[11] No corrections for extinction were made. All calculations were carried out on a Zenith 386 running UNIX V.3 at the University of Calgary with the program package XTAL.[12]

X-ray Structural Analysis of $[Ph_2P(NH)_2]_2Se$, 5. Pale yellow crystals of **5** were formed when a solution of **1a** was heated at reflux in toluene and then allowed to stand for several weeks at room temperature. A suitable yellow, block-shaped crystal (0.27 × 0.36 × 0.43 mm) was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20 < 2\theta < 30$, corresponded to a primitive monoclinic cell. The systematic absences of $h0l$, $h \neq 2n$, and $0k0$, $k \neq 2n$, uniquely determined the space group to be $P2_1/a$ (No. 14). The data were collected using the $\omega/2\theta$ scan technique to a maximum 2θ value of 50.0°. No decay correction was necessary. Crystallographic data for **5** are summarized in Table IV. An empirical absorption correction using the program DIFABS[8] was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[13] and refined by full-matrix least-squares calculations using SHELX76.[14] The non-hydrogen atoms were refined anisotropically. The final values of the refined positional parameters are given in Table V. Hydrogen atoms were included but not refined. Tables of experimental details, calculated hydrogen atom positions, and thermal parameters are available as supplementary material for this paper. Atomic scattering factors were taken from refs 9 and 10, and anomalous dispersion effects were included in F_c.[11] All steps in the data reduction were performed using teXsan.[15]

Results and Discussion

Synthesis of 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et, Ph). The slow addition of $Ph_2PN_2(SiMe_3)_3$ to a solution of an organoselenium trichloride in acetonitrile at room temperature produces the *Se,Se'*-diorganotetraphenyldiphosphadiselenatetrazocines **1a–c** as odorless white solids, which are readily purified by washing with acetonitrile. The derivatives **1a,b** are soluble in dichloromethane, but **1c** is very sparingly soluble in this solvent. The yield of the *Se,Se'*-diphenyl derivative is >90%, while the yields of **1a,b** are somewhat lower, 56% and 86%, respectively, and the formation



$$2Ph_2P(=NSiMe_3)N(SiMe_3)_2 + 2RSeCl_3 \ (R = Me, Et, Ph) \xrightarrow{-6Me_3SiCl} \textbf{1a}, \textbf{1b} \text{ or } \textbf{1c} + \textbf{4} \quad (1)$$

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of **1a,b** is accompanied by small amounts (11% and 7%, respectively) of the 1,5-diphosphadiselenatetrazocine, **4**, which is readily identified by its anomalously low-field ^{31}P NMR chemical shift (113.4 ppm).[4,16] It has not been established whether Se-dealkylation occurs prior to or during the cyclocondensation process.[17] Attempts to make derivatives of **1c** with alkyl substituents on phosphorus by the reaction of $RR'PN_2(SiMe_3)_3$ (R = R′ = Me; R = Me, R′ = Ph) with $PhSeCl_3$ produced PhSeSePh in virtually quantitative yield.

The heterocycles **1a–c** are obtained as white solids, which are stable toward exposure to air for several minutes. However, the *Se,Se′*-dialkyl derivatives **1a,b** undergo a remarkable solid-state transformation upon storage under an inert atmosphere for several weeks (vide infra). All three derivatives decompose on heating above ca. 150 °C to give a red melt. In the case of **1c** slow thermal decomposition at 140 °C over a period of 1 week produces diphenyl diselenide and cyclophosphazenes.

$$\mathbf{1c} \longrightarrow Ph_2Se_2 + {}^{2}/_{n}\,(Ph_2PN)_n \quad (n = 3, 4) \qquad (2)$$

Spectroscopic Characterization of 1,5-$Ph_4P_2N_4Se_2R_2$. The ^1H, ^{31}P, and ^{77}Se NMR data for **1a–c** are summarized in Table I. The ^1H NMR spectra of **1a,b** show the expected resonances for Se–CH_3/C_2H_5 and P–C_6H_5 protons in the appropriate intensity ratio. The ^{77}Se NMR spectra of **1a,b** consist of 1:2:1 triplets at 888 and 896 ppm, respectively, consistent with the expected coupling of selenium with two equivalent phosphorus atoms. The values of ^2J(Se–P) are 86 and 61 Hz, respectively, which is within the observed range of 28–87 Hz for two-bond ^{31}P–^{77}Se coupling constants in unsaturated PNSe compounds.[18] The ^{31}P NMR spectra of all three derivatives **1a–c** display singlets in the region 32–34 ppm, but the ^{77}Se satellites were not resolved.

The FAB mass spectrum of **1a** displays a molecular ion at *m/e* 616 with the appropriate isotopic distribution for a molecule containing two selenium atoms. The electron impact (70 eV) mass spectra of **1a–c** are dominated by the formation of $R_2Se_2^{\bullet+}$ and its fragment ions. The infrared spectra exhibit strong absorptions in the regions 1060–1110 and 950–970 cm^{-1}, which are attributed to P–N and Se–N stretching vibrations, respectively. Collectively the spectroscopic data for **1a,c** are consistent with the proposed cyclic structure, and this conclusion has been confirmed by an X-ray structural determination of **1a**.

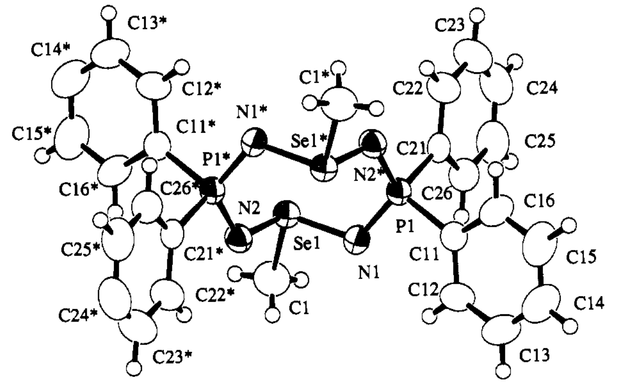

Figure 1. ORTEP plot for 1,5-$Ph_4P_2N_4Se_2Me_2$, **1a**.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 1,5-$Ph_4P_2N_4Se_2Me_2$, **1a**

	Distances		
P(1)–N(1)	1.623(3)	Se(1)–C(1)	1.913(5)
N(1)–Se(1)	1.778(3)	P(1)–C(11)	1.804(4)
Se(1)–N(2)	1.776(3)	P(1)–C(21)	1.814(4)
N(2)–P(1)	1.592(3)		
	Angles		
N(2′)–P(1)–N(1)	120.8(1)	N(1)–Se(1)–C(1)	94.9(2)
P(1)–N(1)–Se(1)	116.0(2)	N(2)–Se(1)–C(1)	95.8(2)
N(1)–Se(1)–N(2)	105.0(2)	C(11)–P(1)–C(21)	104.5(2)
Se(1)–N(2)–P(1′)	118.3(2)		

X-ray Crystal Structure of 1,5-$Ph_4P_2N_4Se_2Me_2$, 1a. The crystal structure of **1a** was reported in the preliminary communication of this work.[4] More details are given here in order to give some background information for the discussion of the solid-state isomerization of **1a,b** (vide infra). The molecular geometry and atomic numbering scheme for **1a** are shown in Figure 1. Selected bond lengths and bond angles are summarized in Table VI. The eight-membered $P_2N_4Se_2$ ring adopts a chair conformation in which the two NPN units are planar to within 0.054(3) Å. The two selenium atoms are displaced on either side of the centrosymmetric ring by 1.073(2) Å, and the two exocyclic methyl groups occupy axial positions. The related heterocycle 1,5-$Ph_4P_2N_4S_2Ph_2$ has a similar structure in which the sulfur atoms lie 0.938(5) Å on either side of the least-squares plane through P_2N_4.[19] The mean Se–N bond length of 1.777(3) Å is similar to values found for *d*(Se(IV)–N) in related unsaturated, six-membered ring systems.[20] A notable feature of Se–N heterocycles, including Se_4N_4,[21] is the existence of strong intermolecular Se–N interactions.[20b] However, the closest *intermolecular* contacts in **1a** are Se–N distances of 3.362(2) and 3.483(3) Å, which do not represent significant Se–N interactions; cf. the sum of the van der Waals radii for selenium and nitrogen (3.36 Å).[22]

Solid-State Isomerization and Dealkylation of 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et). When solid samples of **1a** or **1b** are stored under the dry, nitrogen atmosphere of a glovebox for several weeks, the white color of these solids slowly changes to peach. The derivative **1c** undergoes no observable change in the solid state after 1 year. The ^{31}P NMR spectra of these peach-colored solids in dichloromethane reveal that **1a,b** have been completely transformed into two new products. In both cases the separation of these products was achieved by extraction with acetonitrile, which dissolves the minor product and leaves an essentially pure sample of the major product. The major products were identified as **2a,b**, the 1,3-isomers of **1a,b**, respectively, on the basis of analytical (CHN) and spectroscopic data.

The derivatives **2a,b** have physical properties markedly different from those of their 1,5-isomers. They are peach-colored, extremely malodorous solids which have higher solubilities in organic solvents than **1a,b**. The ^1H NMR spectra of **2a,b** reveal the presence of phenyl and alkyl groups in the ratio 2:1, but the chemical shifts are virtually indistinguishable from those of their 1,5-isomers. However, the ^{31}P NMR spectra of **2a,b** exhibit singlets that are ca. 11 ppm upfield from those of **1a,b**. Furthermore, the ^{77}Se NMR spectra of **2a,b** show resonances that are 44 and 27 ppm upfield, respectively, from those of the corresponding 1,5-isomers and there is a marked difference in the fine structure of these resonances. The signals for **2a,b** consist of complex multiplets as expected for the major isotopomer containing one ^{77}Se atom (natural abundance 7.7%) and mag-

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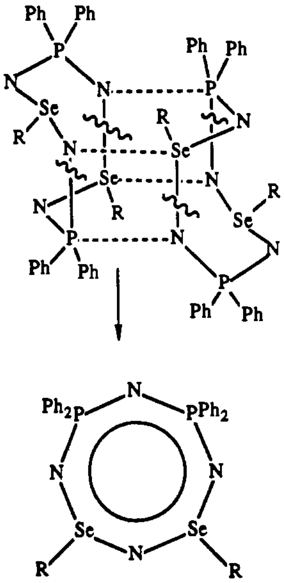

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Figure 2. Possible mode of isomerization of 1,5-$Ph_4P_2N_4Se_2R_2$ into 1,3-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et): ⁓ represents bond-breaking and - - - represents bond formation.

netically inequivalent phosphorus atoms (an AA′X spin system), whereas the ^{77}Se NMR spectra of **1a,b** appear as 1:2:1 triplets due to coupling to two magnetically equivalent phosphorus atoms (an A_2X spin system). The FAB mass spectrum of **2a** displays a molecular ion at m/e = 616 ($Ph_4P_2N_4Se_2Me_2^+$) with the appropriate isotope distribution for a molecule containing two selenium atoms while the electron-impact mass spectra of **2a,b**, like those of **1a,b**, are dominated by $R_2Se_2^{\bullet+}$ and their fragment ions. The infrared spectra of **2a,b** also exhibit significant differences compared to those of **1a,b**. In the P–N stretching region two groups of absorptions are observed at 1100–1170 and 990–1070 cm^{-1} for the 1,3-isomers whereas only one set of bands attributable to ν(P–N) at 1060–1110 cm^{-1} is found for the 1,5-isomers. This dissimilarity presumably reflects the two different types of P–N bonds present in the 1,3-isomers. Small shifts are also observed in the bands assigned to ν(Se–N), which occur at 890–920 cm^{-1} for **2a,b** cf. 950–970 cm^{-1} for **1a,b**, implying that the Se–N framework is weaker in the 1,3-isomers.

Collectively, these spectroscopic data, together with the elemental analyses, establish the identity of the major products of the solid-state transformation of **1a,b** as 1,3-$Ph_4P_2N_4Se_2Me_2$, **2a**, and 1,3-$Ph_4P_2N_4Se_2Et_2$, **2b**, respectively. The minor, acetonitrile-soluble, product was identified 1,3-$Ph_4P_2N_4Se_2$, **3**,[23] which was shown, in a separate experiment, to result from the slow dealkylation of **2a** or **2b** in the solid state at room temperature. Compound **3** was obtained as a yellow solid and identified on the basis of analytical (CHN) and spectroscopic data. The ^1H NMR spectrum shows only signals for aromatic protons at 7.3–8.0 ppm. The ^{31}P NMR spectrum exhibits a singlet at 18.5 ppm [cf. $\delta(^{31}P)$ 18.7 ppm for 1,3-$Ph_4P_2N_4S_2$].[24] The ^{77}Se NMR spectrum exhibits a multiplet at 1356 ppm as expected for the major isotopomer of **3** containing one ^{77}Se atom and two magnetically inequivalent phosphorus atoms. This information and the fact that the same compound is obtained from both **2a,b** establish the identity of the minor product of the decomposition of **1a,b** as 1,3-$Ph_4P_2N_4Se_2$, **3**.

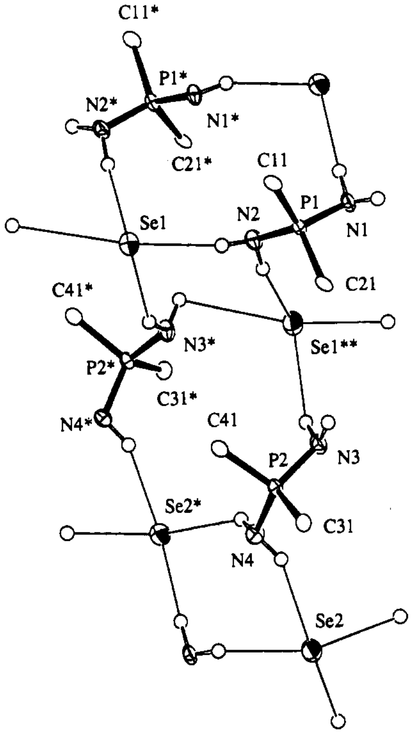
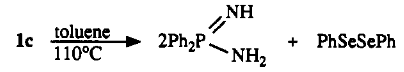


Figure 3. ORTEP plot for $[Ph_2P(NH_2)_2]_2Se$, **5**. The symmetry codes are $^1/_2 + x - 1$, $^1/_2 - y$, z for a single asterisk and $^1/_2 + x$, $^1/_2 - y$, z for a double asterisk.

Mechanism of Isomerization of 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et). Ring expansion and ring contraction reactions are prominent features of sulfur–nitrogen chemistry,[25] but there is only one example of a ring isomerization, viz. the *quantitative*, room-temperature conversion of the 5-methyl-1,3,2,4-dithiadiazolyl radical into the corresponding 2,3,1,4-isomer, which occurs by an intermolecular association.[26] A remarkable feature of the *solid-state* transformation of **1a**/**1b** is the production of **2a**/**2b** and **3** in *essentially quantitative*, combined yields. This observation suggests an intermolecular process for the isomerization, and one possibility is illustrated in Figure 2. We note, however, that this mode of association invokes a substantial distortion of the chair conformation of the $P_2N_4Se_2$ ring and there is no indication of close intermolecular Se–N contacts in the X-ray crystal structure of **1a**. Finally, the conversion of **1a**/**1b** into **2a**/**2b** involves breaking two P–N and two Se–N bonds and forming another two P–N and two Se–N bonds. Thus the reason for the thermodynamic preference for the 1,3-isomers is unclear.

Thermal Decomposition of 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et, Ph) in Solution. In an unsuccessful attempt to follow the kinetics of the isomerization process, solutions of **1a–c** were heated in toluene in reflux.[27] Under these conditions all three derivatives are converted to $Ph_2P(NH)(NH_2)$ within 15 min (**1b**), 2 h (**1a**), or 60 h (**1c**), as determined by ^{31}P NMR spectroscopy. Dialkyl/aryl selenides were identified as the other products by ^{77}Se NMR spectroscopy (eq 3). The same decomposition occurred in dichloromethane solutions of **1a–c** after 3–4 days at room temperature.[27]



$$\mathbf{1c} \xrightarrow[110^{\circ}\text{C}]{\text{toluene}} 2\text{Ph}_2\text{P}\begin{matrix}\nearrow \text{NH}\\ \searrow \text{NH}_2\end{matrix} + \text{PhSeSePh} \tag{3}$$

X-ray Structural Analysis of $[Ph_2P(NH_2)_2]_2Se$, 5. When a toluene solution of $Ph_2P(NH)(NH_2)$ and MeSeSeMe formed by

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[23] Tetraalkyl derivatives of compound **3** have also been obtained, together with 1,5-$R_4P_2N_4Se_2$, from the reaction of $R_2PN_2(SiMe_3)_3$ (R = Me, Et) with a mixture of Se_2Cl_2 and $SeCl_4$ (Se:Cl = 1:3): Chivers, T.; Doxsee, D. D.; Parvez, M. *Inorg. Chem.*, preceding paper in this issue.

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[27] Although trace amounts of residual water in the solvents may account for the decomposition represented by eq 3 and/or for the formation of **5**, the solvents were dried by standard procedures and distilled before use and we have been unable to identify any selenium–oxygen species that might be expected to result from hydrolysis.

Table VII. Bond Lengths (Å) and Bond Angles (deg) for $[Ph_2P(NH_2)_2]_2Se$, **5**

	Bond Distances		
N(1)–P(1)	1.628(4)	N(3)–P(2)	1.617(4)
N(2)–P(1)	1.617(4)	N(4)–P(2)	1.614(4)
C(11)–P(1)	1.800(3)	C(31)–P(2)	1.794(3)
C(21)–P(1)	1.799(3)	C(41)–P(2)	1.789(3)
	Bond Angles		
N(2)–P(1)–N(1)	107.6(2)	C(41)–P(2)–N(4)	106.4(2)
C(11)–P(1)–N(1)	114.0(2)	C(41)–P(2)–C(31)	112.6(2)
C(11)–P(1)–N(2)	107.2(2)	C(12)–C(11)–P(1)	122.6(1)
C(21)–P(1)–N(1)	106.1(2)	C(16)–C(11)–P(1)	117.2(1)
C(21)–P(1)–N(2)	115.0(2)	C(22)–C(21)–P(1)	118.4(1)
C(21)–P(1)–C(11)	107.2(1)	C(26)–C(21)–P(1)	121.6(1)
N(4)–P(2)–N(3)	122.5(2)	C(32)–C(31)–P(2)	122.2(1)
C(31)–P(2)–N(3)	105.0(2)	C(36)–C(31)–P(2)	117.8(1)
C(31)–P(2)–N(4)	105.0(2)	C(42)–C(41)–P(2)	118.5(1)
C(41)–P(2)–N(3)	105.6(2)	C(46)–C(41)–P(2)	121.5(1)
	Interactions of Se^{2} Ions[a]		
Se(1)···H(N21)	2.43	Se(2)···H(N11)a	2.35
Se(1)···H(N22)a	2.39	Se(2)···H(N12)d	2.41
Se(1)···H(N31)c	3.04	Se(2)···H(N41)	2.45
Se(1)···H(N32)a	2.63	Se(2)···H(N42)b	2.55
H(N21)···Se(1)···H(N22)a	108	H(N11)a···Se(2)···H(N12)c	105
H(N21)···Se(1)···H(N31)c	165	H(N11)a···Se(2)···H(N41)	149
H(N21)···Se(1)···H(N32)a	83	H(N11)a···Se(2)···H(N42)b	79
H(N22)a···Se(1)···H(N31)c	71	H(N12)c···Se(2)···H(N41)	71
H(N22)a···Se(1)···H(N32)a	113	H(N12)c···Se(2)···H(N42)b	151
H(N31)c···Se(1)···H(N32)a	111	H(N41)···Se(2)···H(N42)b	90

[a] The following symmetry codes are applied: a, $^1/_2 + x - 1$, $^1/_2 - y$, z; b, $^1/_2 + x$, $^1/_2 - y$, z; c, $1 + x$, y, z; d, x, y, $z - 1$.

the decomposition of **1a** (vide supra) was left at room temperature for several weeks, pale yellow crystals of $[Ph_2P(NH_2)_2]_2Se$, **5**, were produced.[27] An X-ray structural determination of **5** revealed an ionic structure in which the Se^{2-} anions are strongly hydrogen-bonded to four different $Ph_2P(NH_2)_2^+$ cations. An ORTEP plot of **5** giving the atomic numbering scheme is displayed in Figure 3. Pertinent bond lengths and bond angles are summarized in Table VII. The four unique Se--HN distances fall within the range 322–330 pm, which is significantly smaller than the corresponding hydrogen bond distances in selenoureas [*d*(Se--HN) = 351–383 ppm][28] or 2,4-diselenouracil [*d*(Se–HN)] = 347–375 pm].[29] However, similar Se--HN distances (330.5 pm) have been found in the related salt $[N(PMe_2NH_2)_2]_2Se$.[23]

Conclusion

Heterocycles of the type 1,5-$Ph_4P_2N_4Se_2R_2$ are readily obtained in high yield from the cyclocondensation reaction of $Ph_2PN_2(SiMe_3)_3$ with $RSeCl_3$ (R = alkyl, aryl). The formation of the *Se,Se′*-dialkyl derivatives is accompanied by small amounts of 1,5-$Ph_4P_2N_4Se_2$. The structure of 1,5-$Ph_4P_2N_4Se_2Me_2$ consists of an eight-membered $P_2N_4Se_2$ ring in a chair conformation with no significant intermolecular contacts. Nevertheless, at room temperature the *Se,Se′*-dialkyl derivatives undergo a remarkable *solid-state* transformation into their 1,3-isomers and, subsequently, via dealkylation into 1,3-$Ph_4P_2N_4Se_2$. This process provides a facile (albeit slow) preparation of the novel heterocycles 1,3-$Ph_4P_2N_4Se_2R_2$ (R = alkyl) for which sulfur analogues are unknown. The thermolysis of the *Se,Se′*-dialkyl derivatives in solution results in the elimination of diselenides, R_2Se_2, and the eventual formation of the hydrogen-bonded salt $[Ph_2P(NH_2)_2]_2Se$. This decomposition has thwarted attempts to determine the kinetics of the isomerization process. The *Se,Se′*-diphenyl derivative 1,5-$Ph_4P_2N_4Se_2Ph_2$ does not undergo isomerization at room temperature, but prolonged thermolysis at 140 °C produces Ph_2Se_2 and cyclophosphazenes.

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Supplementary Material Available: Listings of crystal data and details of the structure determinations, hydrogen atom parameters, and anisotropic thermal parameters for **1a** and **5** and bond lengths, bond angles, and dihedral angles for **1a** and a packing diagram for **1a** (12 pages). Ordering information is given on any current masthead page.

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